

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

N8323-EAS

U.S. APPLICATION NO. (If known, see 37 CFR 1.52)

10/088441

INTERNATIONAL APPLICATION NO.

PCT/US00/40921

INTERNATIONAL FILING DATE

18 September 2000

PRIORITY DATE CLAIMED

17 September 1999

TITLE OF INVENTION: THERMODYNAMIC ENERGY CONVERSION DEVICES AND METHODS USING A  
DIAMOND-BASED ELECTRON EMITTER

APPLICANT(S) FOR DO/EO/US

Timothy S. Fisher; Alvin M. Strauss; Jimmy Lee Davidson; Weng Poo Kang

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ has been communicated by the International Bureau.
  - c. ☒ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☐ Other items or information:

U.S. APPLICATION NO. (if known) <b>10/088441</b>		INTERNATIONAL APPLICATION NO. <b>PCT/US00/40921</b>		ATTORNEY'S DOCKET NUMBER <b>N8323-EAS</b>	
21. <input checked="" type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. . . . . <b>\$1040.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . . <b>\$890.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . <b>\$740.00</b>  International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . <b>\$710.00</b> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . <b>\$100.00</b> <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS PTO USE ONLY</b>          <div style="border: 1px solid black; width: 100%; height: 100%;"></div>	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	29 - 20 =	9	x \$18.00	\$ 162.00	
Independent claims	8 - 3 =	5	x \$84.00	\$ 420.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$280.00	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$ 1292.00</b>	
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				+ \$ {646}	
<b>SUBTOTAL =</b>				<b>\$ 646.00</b>	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
<b>TOTAL NATIONAL FEE =</b>				<b>\$ 646.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$ 646.00</b>	
				Amount to be refunded:	\$
				charged:	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>646.00</u> to cover the above fees is enclosed  b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.  c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-0035</u> . A duplicate copy of this sheet is enclosed.  d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. <b>Credit card information should not be included on this form.</b> Provide credit card information and authorization on PTO-2038.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:  <div style="display: flex; justify-content: space-between;"> <div style="width: 60%;">                     Emily A. Shouse                      Waddey &amp; Patterson                      414 Union Street, Suite 2020                      Nashville, TN 37219                 </div> <div style="width: 35%; text-align: right;"> <div style="border-bottom: 1px solid black; margin-bottom: 5px;"> </div>                     SIGNATURE   <div style="border-bottom: 1px solid black; margin-bottom: 5px;">Emily A. Shouse</div>                     NAME   <div style="border-bottom: 1px solid black; margin-bottom: 5px;">44,336</div>                     REGISTRATION NUMBER                 </div> </div>					

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Fisher, et al
Serial No.:	Not yet assigned
Filed:	Not yet assigned
For:	Thermodynamic Energy Conversion Devices And Methods Using A Diamond- Based Electron Emitter
Group Art Unit:	Not yet assigned
Examiner:	Not yet assigned
Attorney's Docket No.	N8323-EAS

PRELIMINARY AMENDMENT

Box PCT  
Commissioner of Patents  
and Trademarks  
Washington, DC 20231

Dear Sir:

Applicant is filing this Preliminary Amendment upon entry  
into the National Stage of PCT/US00/40921.

No amendment has been made to the claims. Only a  
sequential numbering problem has been corrected.

[illegible]

34. The energy conversion device of claim 27, the diamond emitter including dopants that produce band bending via space charge accumulation.

35. The energy conversion device of claim 27, the dopant selected from a dopant group including as nitrogen, phosphorous, and sulfur-hydrogen.

36. An electronic cooling device, comprising:  
a cathode comprising at least one emitter structure on a base;  
and  
an anode positioned over and spaced apart from the cathode by a vacuum space,  
a biasing energy supply adapted to bias the cathode to anode separation, the bias of sufficient potential to cause electron emission from the base electrode through the cathode into the conduction band, then through the vacuum and deposition in the anode;  
the emitter structure including a diamond microtip emitting portion.

37. The electronic cooling device of claim 36, the diamond microtip emitting portion including a geometric tip enhancement for enhancing band bending.

38. An electronic cooling device, comprising:  
a cathode comprising at least one emitter structure on a base, the emitter structure including a diamond microtip emitter extending upwardly from and formed integral to a diamond substrate having a top surface;

an anode layer spaced apart from the emitter and suspended above the diamond substrate by a first insulating layer extending upwardly from the top surface of the diamond substrate;

a porous gate positioned above and spaced apart from the diamond microtip, supported by a second insulating layer extending upwardly from a top surface of the anode layer; and

a biasing energy supply adapted to bias the anode and the gate separation, the bias of sufficient potential to cause electron emission from the base electrode through the cathode into the conduction band, then through the vacuum and deposition in the anode.

39. The device of claim 38, the porous gate is constructed in a grid arrangement.

40. The device of claim 38, the porous gate is constructed in an annular gate structure adapted to provide appropriate electrical conditions for cathode emission, while also providing a path to the anode.

41. The device of claim 38, wherein the bias between the cathode and the anode is maintained at a higher level than that of the bias between the cathode and the gate, but the bias between the cathode and the anode still allows electrons emitted from the cathode to reach the anode.

42. A method for energy conversion using a diamond microtip cathode separated from an anode by a vacuum space, the method comprising:

shifting the field emission band with a positive voltage bias on the anode to narrow the potential barrier width to increase the

probability of quantum tunneling to increase field emission and produce a transfer of thermal energy from the cathode to the anode.

43. The method for energy conversion of claim 42, wherein shifting the field emission band occurs in the cathode.

44. The method for energy conversion of claim 42, the shifting occurring near the base-electrode/cathode interface

45. The method for energy conversion of claim 42, wherein shifting the field emission band occurs in the vacuum.

46. The method for energy conversion of claim 42, the shifting occurring near sp<sup>2</sup>-bonded elements of the polycrystalline structure.

47. The method for energy conversion of claim 42, the shifting occurring at the cathode/vacuum barrier

48. The method for energy conversion of claim 42, further comprising:

decreasing the resistance to electron flow between the cathode and anode through the use of a gate electrode designed to extract electrons from the cathode while allowing emitted electrons to bypass the gate.

49. An energy conversion structure, comprising:

a biased diamond microtip emitter thermally and electrically connected to a base and spaced from an anode by a vacuum gap, the biased microtip emitter forming curved energy bands adapted to produce a net energy transfer to an anode.

50. The energy conversion structure of claim 49, the net energy transfer manifest as cooling of the base.

51. The energy conversion structure of claim 49, the net energy transfer manifest as power generation with an electrical potential between the anode and the base.

52. A step for improving efficiency for an energy conversion device using a base electrode and a diamond emitter cathode, the step for improvement comprising:

providing geometric enhancement adapted to increase the local electric field at the interface between the base electrode and the diamond cathode.

53. A diamond emitter energy conversion device adapted to provide power to an external circuit, comprising:

a cathode with a microtip structure, the cathode adapted to support a high density of energetic electrons and further adapted to be electrically connected to the external circuit;

an anode spaced from the cathode and adapted to be electrically connected to the external circuit;

an annular gate electrode adapted to provide a low potential field sufficient for emission of electrons from the cathode tip to the anode by bypassing the annular gate; and

a biasing energy supply adapted to bias the anode and the gate separation, the bias of sufficient potential to cause electron emission from the base electrode through the cathode into the conduction band, then through the vacuum and deposition in the anode.

54. A method for increasing efficiency of energy converters utilizing a thermal differential across a structure including a base



connected to a cathode, the cathode separated from an anode by a vacuum space, the cathode including a diamond microtip emitter, comprising:

enhancing band bending potential of the structure during construction of the cathode and anode structure.

55. The method of claim 54, further comprising:

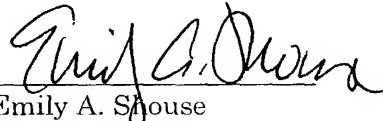
providing a gate electrodes during construction, the gate electrode adapted to reduce the required voltage for field emission within the structure.

#### REMARKS

Claims 1-26 have been canceled and renumbered as Claims 27-55 to correct a sequential numbering problem. Thus, 29 claims are pending in the application. The claims are otherwise unchanged.

The Commissioner is authorized to charge any deficiency or credit any overpayment associated with the filing of this Preliminary Amendment to Deposit Account 23-0035.

Respectfully submitted,



Emily A. Shouse  
Registration No. 44,336  
WADDEY & PATTERSON  
Bank of America Plaza  
414 Union Street, Suite 2020  
Nashville, TN 37219  
(615) 242-2400

ATTORNEY FOR APPLICANT

1.

DESCRIPTIONTHERMODYNAMIC ENERGY CONVERSION DEVICES AND  
METHODS USING A DIAMOND-BASED ELECTRON EMITTER5 TECHNICAL FIELD

The present invention relates generally to energy conversion devices, and more particularly, this invention pertains to the use of diamond-based electron emitters in thermodynamic energy conversion devices.

10

BACKGROUND ART

The need for efficient, reliable, and cost-effective small-scale energy conversion devices is increasing due to the downsizing of commercial and military products that require either electrical power or compact cooling. An example of a product that requires both of these is a portable infrared detector, which is used for both military and law-enforcement applications. This device requires portable electrical power to drive electronic components as well as a compact cooling system to maintain the temperature of the primary optoelectronic sensor (e.g., a silicon microbolometer) within a narrow range at or below ambient. Similar needs for efficient, small-scale cooling and/or power generation will persist for many future engineering applications.

Small-scale cooling systems are increasingly in demand as the need increases to transfer heat from microelectronic components, such as ultra large scale integration (ULSI) devices and laser diode arrays. The 1997 National Technology Roadmap for Semiconductors indicates that surface cooling rates in excess of 30 W/cm<sup>2</sup> will be required for sub-100 nm technology while maximum device junction

temperatures will remain at or below 100°C. Further, the cooling systems must be reliable, inexpensive, and manufacturable.

The required cooling capacity can be achieved by a variety of methods, including single- and two-phase fluid flow, air jet  
5 impingement, and both traditional and non-traditional refrigeration schemes. For liquid-flow and air-impingement systems, intricate flow networks and flow-generating mechanisms are required which can limit their practicality. Alternative devices, such as thermoelectric refrigerators, eliminate moving parts by using electrical current to  
10 produce refrigeration. However, room-temperature thermoelectric refrigerators are inefficient, with typical coefficients of performance (COPs) that are about one-third those of ordinary vapor-compression refrigerators. Contemporary research is seeking to improve the efficiency of thermoelectrics.

15 Recently, several researchers have suggested that, in theory, high-efficiency room-temperature refrigeration can be achieved via small-scale electron emission devices. The physical principle of this concept involves thermionic electron emission, whereby hot electrons are ejected over a potential barrier. The primary challenges in  
20 achieving thermionic refrigeration involve finding materials with low potential barriers (i.e., work functions) and minimizing reverse heat transfer.

Field emission provides an alternate means of electron emission whereby electrons tunnel through a potential barrier. Field  
25 emission is particularly appealing because electrical current densities can be significantly larger than those generated by thermionic emission. This extremely high electrical current density suggests that high thermal current densities are possible. Recent work by several groups suggests that, in theory, field emission devices made from  
30 wide-bandgap semiconductors can provide direct cooling.

In addition to cooling applications, compact sources of electrical power (thermal-to-electrical power generation devices) are needed to drive a wide variety of current and future engineering devices. For many applications, electrochemical batteries do not provide sufficient  
5 power or energy storage capacity. Other power sources, such as liquid fuels and radioactive elements, possess high energy density but require a means of converting thermal power to electrical form. Like compact cooling systems, the minimization of moving parts is essential to the creation of a new generation of small-scale power  
10 generation devices.

Compact thermoelectric and thermionic systems can reliably convert thermal to electrical energy with no moving parts. Several United States patent are directed towards these devices including: United States Patent No. 6,103,298, issued to Edelson et al., on Aug.  
15 15, 2000; United States Patent No. 6,064,137, issued to Cox, on May 16, 2000; United States Patent No. 6,055,815, issued to Peterson, on May 2, 2000; United States Patent No. 6,039,471, issued to Wyland, on March 21, 2000; United States Patent No. 5994638, issued to Edelson, on Nov. 30, 1999; United States Patent No. 5,984,752, issued  
20 to Tanaka et al. on Nov. 16, 1999; United States Patent No. 5,981,071, issued to Cox, on Nov. 9, 1999; United States Patent No. 5,874,039, issued to Edelson, on Feb. 23, 1999; United States Patent No. 5,777,427, issued to Tanaka et al., on July 8, 1998; United States Patent No. 5,722,242, issued to Edelson, on Mar. 3, 1998; United  
25 States Patent No. 5,712,448, issued to Vandersande et al., on January 27, 1998; and United States Patent No. 5,675,972, issued to Edelson, on Oct. 14, 1997. These patents are hereby incorporated by reference. However, as described previously, these systems are susceptible to low efficiency and materials limitations.

What is needed, then, is an improved method for field emission energy conversion which offers the possibility of improved power densities and high thermal efficiency as compared to competing approaches, and an improved method for field emission as a  
5 mechanism for power generation.

#### DISCLOSURE OF THE INVENTION

The present invention describes specific features that enable or enhance direct energy conversion for uses such as cooling and power generation. The central element of the present invention involves the  
10 issue of energy-band bending that enables the selective emission of high-energy electrons.

The preferred embodiments teaches the use of band bending to enable or enhance energy conversion. Three different band bending methods are described. The first involves the use of geometric tip  
15 enhancement. The second involves the inclusion of graphite-like (sp<sup>2</sup>-bonded) molecular structures within the polycrystalline film. These two features produce band bending via small geometric features, such as tips and filaments, as governed by electrostatic theory. The third involves the incorporation of p- and n-type dopants that produce band  
20 bending via space charge accumulation.

Fig. 1a shows band diagrams for field emission from diamond cathodes in an unbiased state at thermal equilibrium.

Fig. 1b shows band diagrams for field emission from diamond cathodes under bias with tunneling into and from the conduction  
25 band.

Fig. 2 shows a closer view of a field emission process with and without band bending.

Fig. 3 shows refrigeration enhancement using a gate electrode with a band diagram for field emission from a gated diamond cathode  
30 in the biased state.

5.

Fig. 4 shows an annular gate structure surrounding a diamond-tip emitter cathode.

Fig. 5 shows a band diagram for a gated power generation device.

5 Fig. 6 shows a schematic of a direct refrigeration device.

Fig. 7 shows a predicted cooling capacity as a function of applied electric field, field enhancement factor  $\beta$ , and temperature.

Fig. 8 shows a schematic of a direct power generation device.

10 Fig. 9 shows a predicted thermal efficiency of standalone power generation by field emission as a function of hot-side temperature.

Fig. 10 shows a predicted thermal efficiency of topping cycle power generation by field emission as a function of hot-side temperature.

## 15 BEST MODE FOR CARRYING OUT THE INVENTION

The present invention teaches the manipulation of potential barriers, e.g., band bending, to produce enhanced field emission for the purpose of energy conversion. A grid arrangement is also taught for enhanced field emission. In contrast to the prior art teachings  
20 regarding thermionic emission over a potential barrier, the present invention utilizes field emission, which involves quantum tunneling through a potential barrier. The basic understanding for the patterned and designed methods for construction of the integral, common and monolithic substrate and emission cathodes for the  
25 present invention are taught in the prior incorporated applications. These prior teachings include uniform tip shape, length, grain size, sp<sup>2</sup> control, p doping and n doping. It is assumed that the reader has read and understands the basis of those references in the following teachings of the present invention. The present invention builds upon

these teachings by teaching methods for band bending to provide for direct refrigeration and electrical power generation.

Three mechanisms may be used to encourage band bending to enable or enhance energy conversion. The first involves the use of geometric tip enhancement, an example is shown in Figure 3. The second involves the inclusion of graphite-like (sp<sup>2</sup>-bonded) molecular structures within the polycrystalline film. These two features produce band bending via small geometric features, such as tips and filaments, as governed by electrostatic theory. The third involves the incorporation of p- and n-type dopants that produce band bending via space charge accumulation. Considerations are directed to diamond emitters that preferentially emit a high-energy distribution of electrons to produce an energy conversion effect.

The origin of the tunneling electrons can be the valence band or conduction band depending on geometric and material properties. Emission has been shown to originate from the diamond's valence band in studies on single-crystal diamond and tetrahedral amorphous carbon. However, some forms of polycrystalline diamond grown by chemical vapor deposition emit electrons from the conduction band, aided by a high content of graphite-like (so-called sp<sup>2</sup>) bonding.

Tunneling into the conduction band is shown schematically in the band diagrams of Fig. 1 for field emission from diamond cathodes. Fig. 1(a) shows the unbiased state, with slight band bending due to space charge effects.  $E_C$  is the conduction band energy,  $E_V$  is the valence band energy. The band gap,  $E_g = E_C - E_V$ , of diamond is 5.5 eV, and the difference between the base electrode's Fermi energy and the cathode's valence band energy is typically  $E_{FB} - E_V = 1.4$  eV, which is the energy associated with grain boundaries. Cathode doping, such as nitrogen, phosphorous, sulfur-hydrogen, and others, can alter this energy difference. The effective work function  $\phi_{eff}$  is dictated by the

vacuum energy level,  $E_{\text{vac}}$ . This work function represents the electron energy required to exceed all potential barriers. The parameter  $\chi = E_{\text{vac}} - E_{\text{C}}$  is the electron affinity and represents the energy required to eject an electron from the conduction band into vacuum. Numerous recent studies indicate that  $\chi$  is negative when the diamond surface is terminated by hydrogen, although it is shown positive in Fig. 1. This negative electron affinity can significantly enhance emission.

An applied bias may be placed between the base electrode and the anode or the anode and the gate in a gated structure. At sufficiently high biases, the electrons will emit from the base electrode through the cathode into the conduction band, then through the vacuum and deposit in the anode. Note that tunneling may also occur through the barrier between the cathode and the vacuum. By comparing the band diagrams of figure 1(a) and 1(b) one can note that band bending allows for thus use of lower vacuum requirements that required in the prior art.

Under a voltage bias, positive on the anode, the electric field causes the bands in the cathode and vacuum to shift, as shown in Fig. 1(b). Near the base-electrode/cathode interface or near sp<sup>2</sup>-bonded elements of the polycrystalline structure, significant band bending narrows the potential barrier width  $w$ . This narrow barrier increases the probability of quantum tunneling, and field emission occurs. A second tunneling process may also occur at the cathode/vacuum barrier for  $\chi > 0$ . Note that the average energy exchange,  $\phi_{\text{ave}}$ , of tunneled electrons can be positive relative to the base electrode's Fermi level due to the triangular-like shape of the barrier. Emitted electrons originate from the high-energy tail of the Fermi-Dirac electron distribution at non-zero absolute temperatures and are transported quasi-ballistically through the cathode into vacuum. In effect, only high-energy electrons are emitted, and the electrical



current caused by this preferential emission produces a commensurate transfer of thermal energy from the cathode to the anode.

Figure 1(b) shows a biased emitter with curved energy bands. A closer view of a field emission process with and without band bending appears in Figure 2. Figure 2 shows two emission processes that, by assumption, produce the same electrical current flows. Despite the fact that the electrical current flows of the two devices are equal, the average energy of electrons emitted through the curved barrier is higher than that of the linear barrier. Prior art devices presume a linear energy barrier, as evidenced by their use of a traditional Fowler-Nordheim equation. Emitted electrons must be replaced by an equal number of electrons to preserve charge continuity. However, in the present invention, these replacement electrons have energies below the average energy of emitted electrons. The replacement energy will, on average, be near the incident energy level, e.g., the Fermi energy of a metal. Thus, the emission process produces a net energy transfer that can be manifest as cooling or power generation.

The physics of field emission have been described in detail by Good and Muller and more recently by Chung et al. The development below provides some of the major results that are central to the present invention. The emission current density  $J_E$  takes the form:

$$J_E = \frac{4\pi me}{h^3} \int_0^\infty \int_0^E f(E) D(E_x) dE_x dE \quad (1)$$

where  $h$  is Planck's constant,  $m$  is the electron rest mass,  $f$  is the Fermi-Dirac energy distribution, and  $D$  is the quantum tunneling transmission coefficient. As described by Muller and Good, the transmission coefficient  $D(E_x)$  is based on an expansion of the quantum tunneling probability, including the effects of the electrode-

semiconductor work function ( $\phi = V_0 - E_{FB}$ ), the local electric field  $F_{local}$  at the interface, and an image charge potential.

To characterize thermodynamic transport, the average energies of emitted electrons ( $E_{ave}$ ), as well as those that replace them  
 5 ( $E_R$ ) must be known. The difference between the two is the electron exchange energy,  $f_{ave} = E_{ave} - E_R$ . The average energy of emitted electrons can be calculated by taking an energy moment of Eq. (1)

$$E_{ave} = \frac{\int_0^\infty \int_0^\infty E f(E) D(E_x) dE_x dE}{\int_0^\infty \int_0^\infty f(E) D(E_x) dE_x dE} \quad (2)$$

As proposed by Chung et al., the average energy of the replacement  
 10 electrons can be calculated as

$$E_R = \frac{\int_0^{E_F} \int_0^\infty E (1 - f(E) + f(E) D(E_x)) dE_x dE}{\int_0^{E_F} \int_0^\infty (1 - f(E) + f(E) D(E_x)) dE_x dE}$$

(3)

The energy of replacement electrons typically falls in the range of 0.1 to 0.2 eV below the Fermi level. This result is extremely important in  
 15 assessing the possibility of direct cooling by field emission, as even emission from slightly below the Fermi level can produce a refrigeration effect when the average replacement energy is below the Fermi level.

Equations (3) and (4) are used to compute the average  
 20 exchange energy  $f_{ave} = E_{ave} - E_R$ . The net thermal energy flux of emitted electrons can then be expressed as

$$J_Q = \phi_{ave} J_E$$

(4)

The heat transfer rate described by Eq. (4) flows from the base electrode, through the cathode and vacuum, and finally to the anode.

The term  $F_{local}$  represents the local electric field at the interface between the base electrode and the diamond cathode, see Fig. 1. This field is greater than the average field, denoted by  $F_{ave}$ , due to geometric enhancement, e.g., micro-nanoscale tips on the cathode emitter, polycrystalline structure (with sp<sup>2</sup> bonding), and cathode doping. The local and average fields are often related by a field enhancement factor  $\beta$  as:

$$F_{local} = \beta F_{ave} \quad (5)$$

This enhancement factor can be very large due to the influence of the emitter geometry, as well as doping and fabrication. The field enhancement factor can be determined from electrical measurements of applied field  $F_{ave}$  and current density  $J_E$ .

### Direct Refrigeration (Cooling)

The fundamental phenomenon described can produce refrigeration.

The flow of thermal energy  $J_Q$  from a lower-temperature cathode to a higher-temperature anode is itself refrigeration. According to the Second Law of Thermodynamics, this process requires the input of energy (power). This 'external' power input is manifest in the biasing of the cathode and anode. The electrical energy input can be calculated as:

$$J_{in} = J_E (E_{FB} - E_{FA}) \quad (6)$$

where the term  $(E_{FB} - E_{FA})$  represents the applied bias, and the term  $J_E$  is the electrical current density. The electrical current creates a thermal current density. The refrigeration efficiency (coefficient of

The basic elements of the refrigeration device can also be configured to create an electrical power generation device. This part of the invention exclusively involves gated emitters as previously described. All energy conversion field emitters require a decreasing potential field in the direction of emission. This process is inherently energy-consuming. However, this energy consumption can be abated or minimized.

One should consider a hot ( $T > 300^\circ\text{C}$ , for example) tip cathode with a correspondingly high density of energetic electrons according to the Fermi-Dirac distribution. An annular gate electrode provides a low potential field sufficient for emission of hot electrons from the cathode tip. Electrons emit toward the anode (bypassing the annular gate) with a total angular spread of  $20\text{-}40^\circ$  from the tip axis. If the cathode and anode are electrically insulated, the system develops an open circuit bias, which ultimately halts the flow of electrons. If instead the cathode and anode are connected by an external circuit, the flow of electrons will continue, and the device produces electric power.

A band diagram for the proposed device is shown in Fig. 5. As shown in figure 5, hot electrons, bolstered in number by the high temperature of the cathode, are emitted into vacuum with an average potential of  $\phi_{\text{ave}}$  above the base electrode's Fermi energy  $E_{\text{FB}}$ . The cathode tips provide the directional orientation of the electrons toward the anode. Electrons with energies greater than  $(E_{\text{FA}} - E_{\text{FB}} + f_{\text{A}})$  will surpass the anode's surface barrier and proceed into the anode with a current density  $J_{\text{E}}$ . Other electrons will flow into the gate and will constitute a loss. The cathode-to-anode power generated by this mechanism is  $J_{\text{E}} * (E_{\text{FA}} - E_{\text{FB}})$ . To minimize losses to the gate, the average energy of emitted electrons must be high, and the anode work function  $f_{\text{A}}$  should be as low as possible. The high average emission energy can be achieved through the combination of the triangular barrier, which is inherent to field emission, and high cathode temperatures, which broaden the Fermi-Dirac electron distribution. Sufficiently low anode work functions ( $> 2\text{ eV}$ ) can be achieved through proper material selection.

## Preferred Embodiments

### Direct Refrigeration

The potential applications for this technology fall into two primary areas--cooling of compact heat sources (e.g., electronic components) and air conditioning/environmental controls. In the former area, the principle advantage is the potential for extremely high cooling densities for high-power, compact electronic devices, such as power diodes and transistors. In the latter area, the principal advantages include the potential for high efficiency, compact size, long-term reliability, and the replacement of traditional air-conditioning and refrigeration systems. In both cases, the cost projections are very favorable when compared to competitive technologies. This concept's potential for high efficiency and elimination of refrigerant fluids would significantly reduce harmful environmental effects, including ozone depletion and greenhouse gas production, that are present in current cooling technology. Fig. 6 shows a schematic of an implementation, with a heat source that is cooled by a field emission device, powered by a direct-current power supply (V). Further enhancement may be implanted through the addition of a gate structure.

Fig. 7 shows predicted field-emission cooling capacities as a function of applied electric field. The parameter  $\beta$  represents the field enhancement factor that enables high emission fluxes at moderate applied fields.  $\beta$ -values of 1300 and 535 have been demonstrated by Vanderbilt's Diamond Technology Group, and a  $\beta$ -value of 2500 is considered to be achievable in the near future. For all levels of field enhancement, cooling capacities greater than 10 W/cm<sup>2</sup>, and some above 1000 W/cm<sup>2</sup>, are predicted. Such a level of direct cooling far surpasses competitive technologies, such as thermoelectrics.

The efficiencies (i.e., coefficients of performance) for field-emission refrigeration are predicted to approach 85% of the Carnot efficiencies. Thus, air-conditioning units based on field-emission technology could be operated at Energy Efficiency Ratios (EERs) above 20. This level of performance significantly exceeds that of the best available central air units, which provide EER values of 10-12. Given that cooling and refrigeration systems account for 41% of the energy consumption in residential and commercial buildings in the U.S., this level of efficiency improvement could have substantial impact across many commercial sectors.

The high cooling density offered by this technology could address important applications in electronics cooling, where heat fluxes greater than 100 W/cm<sup>2</sup> are projected. Further, the technology could readily be applied to novel air conditioning and heat pump devices. At a conservative cooling rate of 10 W/cm<sup>2</sup>, a field emission cooling system would require only 0.03 cm<sup>2</sup> for each Btu/hr of cooling capacity. A 50,000 Btu/hr heat pump or air conditioning system would require a cooling surface area of only 1,500 cm<sup>2</sup> (or 15x15 sq. in.). Thus, a window-sized field emission unit could replace an entire central air conditioning system. Obviously, cooling capacities above 10 W/cm<sup>2</sup> would decrease the required area and the associated costs.

Based on its high efficiency, compact size, and competitive cost projections, field-emission technology could create a new paradigm in cooling and refrigeration. Residential and commercial air conditioning could be implemented in an unobtrusive and decentralized manner. With the addition of simple heat exchangers and fans, such as perhaps ceiling fans, window field-emission air conditioners could be installed in compact form factors. The opportunity for individual room temperature control would provide further energy efficiency advantages. In the field of electronics cooling, field-emission coolers

could be tightly integrated with compact electronic packages due to their compact structure and high energy density.

### Direct Power Generation

5       The proposed technology would address several key areas in the development of new power generation technology. A generic schematic of the concept is shown in Fig. 8. A heat source (e.g., coal, natural gas, solar radiation, radioisotope, etc.) provides thermal energy to the cathode. The cathode then emits electrons past the gate  
10       structure (not shown) to the anode, producing electrical power through a load. The system could be compact (portable) or large (fixed).

      This technology would be well suited for industrial power generation systems. As opposed to coal-fired boiler systems, this  
15       technology is ideal for capturing the high-temperature energy content of combustion. This high-temperature capability could, for example, be utilized as a retrofitted topping cycle in a traditional coal-fired boiler. The field emitter arrays would be placed in proximity to high-temperature zones near the region of combustion with a refractory  
20       material between the combustion region and the diamond field emitters. These devices would then directly convert the high-temperature heat to dc-electricity, and the waste heat would be delivered to the boiler tubes through an appropriate heat exchanger. This approach would take advantage of the projected high efficiency  
25       and capacity of field emission energy conversion over broad temperature ranges.

      A crucial facet of the proposed technology is its ability to operate efficiently and robustly over broad temperature ranges. Fig. 9 contains theoretical predictions of the thermal efficiencies of field  
30       emission energy converters as a function of hot-side temperature over



the range 500°K to 1500°K. The cold-side temperature is assumed to be 350°K. The upper limit on temperature is due to a material limitation of diamond, which graphitizes above approximately 1500°K. The basis model for the calculations in Fig. 9 includes the effects of thermal losses due to thermal radiation between the hot and cold sides. Figure 9 indicates that the proposed technology maintains high efficiency over broad temperature ranges. The predicted efficiency is approximately 85% of the Carnot efficiency, with slightly lower relative efficiency at high temperatures due to the increased effects of thermal radiation losses. Relative to competitive technologies, the predicted efficiencies compare favorably with coal-fired boilers (efficiency  $\approx$  40%) and gas-turbine combined cycles (efficiency  $\approx$  56%) and far exceed those of thermoelectrics (efficiency  $\approx$  10%).

As a topping cycle, the proposed technology could substantially enhance overall efficiency. Fig. 10 shows projected efficiencies for a field-emission topping cycle operating at a cold-side temperature of 840 degrees K (1050 degrees F). The waste heat would be delivered to a typical steam cycle. Figure 10 indicates topping efficiencies in the range of 14-37%, depending on the hot-side temperature. A topping cycle could be developed as a retrofit to existing boilers or designed directly into new boiler concepts.

The high efficiency over a broad temperature range, as shown in Figs. 9 and 10, suggests that field emission energy conversion technology could be implemented in a variety of ways, including as a stand-alone system, a topping cycle, or a bottoming cycle. The technology is inherently compact, and, in contrast to most alternative technologies, contains no moving parts. Hence, the technology possesses inherent capabilities for retrofit systems or for distributed power generation systems, where field reliability is crucial. The

potential thermal energy sources include coal, natural gas, biomass, fuel cells, radioisotopes, and solar radiation, among others.

Field emission energy conversion systems would be mechanically simple, and consequently, could be highly cost effective. Conservative theoretical predictions of generation capacity fall in the range of 10 to above 100 W/cm<sup>2</sup>, depending on temperature conditions. It is estimated that functional field emitter arrays could be produced at a cost of \$1/cm<sup>2</sup> including depreciated capital and recurring fabrication expenses. Thus, the technology could be implemented at a cost of only \$10-100/kW-dc.

The total system costs of field-emission power generators will depend on the application. For standalone, distributed power, estimates show that a traditional dc-to-ac power conversion system (including inverters, circuit breakers, etc.) could be implemented at a cost of approximately \$280/kW, resulting in a total system cost of \$290-380/kW-ac. However, CVD-diamond electronic power conversion components (developed in a parallel research program) could reduce this amount to \$40-80/kW. Thus, a standalone, all-diamond power generation and conversion system could be implemented at a cost of \$50-180/kW-ac for distributed systems (~10 MW). This cost estimate compares very favorably to competitive technologies, including diesel generators (~\$600/kW), gas turbines (~\$500/kW), and fuel cells (>\$1,000/kW).

The proposed technology could also provide significant financial benefits in the development of new coal-fired boilers that include field-emission topping cycles. Consider a field-emission topping cycle that receives heat at 1400 K (2060 F) operating at an efficiency of  $\eta_{\text{topping}} = 35\%$  (see Fig. 8), and a combined steam cycle operating at an efficiency of  $\eta_{\text{steam}} = 40\%$  between 840 K (1050 F) and 350 K (170 F). The overall efficiency for such a system would be

h<sub>overall</sub> = h<sub>topping</sub> + h<sub>steam</sub>(1-h<sub>topping</sub>) = 61%. This level of efficiency would represent a revolutionary improvement over existing technology.

From a cost perspective, new pulverized coal-fired boilers with  
5 modern environmental controls (e.g., scrubbers, selective catalytic  
reduction systems) can be established at a cost of approximately  
\$900/kW-ac. The cost of the topping cycle and associated power  
conversion system is estimated to fall in the range of \$50-180/kW-ac  
while increasing efficiency from 40% to 61%. Note that, in this  
10 scenario, the steam cycle would produce approximately 43% of the  
total energy (primarily because it receives only the waste heat from  
the topping cycle), while the topping cycle would produce 57% of the  
total energy. Thus, the combined system could be implemented at a  
cost of  $C = (\$900/\text{kW-steam}) \cdot 43\% + (\$50-180/\text{kW-topping}) \cdot 57\% =$   
15  $\$415-490/\text{kW-total}$ . The primary reasons for this dramatic reduction  
in cost are that much smaller steam systems would be required and  
that the field-emission technology is inherently inexpensive.

Figure 11 shows the design of the proof of concept experiment  
1100 as used for the present invention. The device includes a cold  
20 plate 1101 thermally coupled to a cathode 1102 spaced from an anode  
1104. The anode 1104 is thermally coupled to a calorimeter 1106  
which includes cooling channels 1108. The cooling channels 1108 are  
flowably coupled to pipes 1110 which provide water pumped from an  
adjustable temperature bath and pump 1112. A voltage potential is  
25 applied by a power supply 1114 through electrical connections 1116  
to the anode 1104 and the cathode 1102. The current flow in the  
electrical connections 1116 is monitored by an ammeter 1118. A  
thermocouple 1120 is connected by couplers 1122 to the cold plate  
1101, cathode 1102, anode 1104, and calorimeter 1106. The cold  
30 plate 1101, cathode 1102, anode 1104, calorimeter 1106 and

Figure 12 shows a simple experiment design 1200 for the concept. The simple experiment includes a cold plate 1202 maintained at 27 degrees C, thermally coupled to a diamond cathode 1204. The diamond cathode 1204 is spaced from an anode 1206 which is thermally coupled to heat spreaders/radiation surfaces 1208. The heat spreaders/radiation surfaces may be cooled by a thick wire 1210 thermally coupled to a heat sink 1212 and cooled by a fan 1214. The anode 1206 and cathode 1204 are electrically connected by electrical connections 1216 such that the anode 1206 and cathode 1204 are biased by a power supply 1218. A thermocouple/RTD 1220 is connected by couplers 1222 to the heat spreaders/radiation surfaces 1208. The heat spreaders/radiation surfaces 1208 may be prepared with high emissivity paint and separated by low conductivity spacers.

Figure 13 of the drawings shows the basic device structure **1300**. The device structure **1300** includes a base electrode (e.g. metal) **1302** connected to a cathode (e.g. wide band gap semiconductor) **1304** and spaced by a vacuum gap **1306** from an anode (e.g. metal) **1308**.

Figure 14 shows the cathode detail 1400 with the cathode containing a micro-structured surface 1406 to enhance emission. The micro-structure surface 1406 includes conical or pyramidal tips 1402.

The gate electrodes 1404 can modulate emission and can reduce the required voltage for emission.

Thus, although there have been described particular embodiments of the present invention of a new and useful  
 5 Thermodynamic Energy Conversion Devices and Methods Using a Diamond-Based Electron Emitter, it is not intended that such references be construed as limitations upon the scope of this invention except as set forth in the following claims.

CLAIMS

What is claimed is:

1. An energy conversion device adapted to enhance field emission, comprising:  
5 a diamond emitter adapted to utilize band bending to emit a high-energy distribution of electrons to produce an energy conversion effect.
2. The energy conversion device of claim 1, the diamond emitter  
10 including a geometric tip enhancement.
3. The device of claim 2, the geometric tip enhancement comprising:  
micro-nanoscale tips on the cathode emitter.  
15
4. The device of claim 2, the geometric tip enhancement comprising:  
a conical tip shape.
- 20 5. The device of claim 2, the geometric tip enhancement comprising:  
a pyramidal tip shape.
6. The device of claim 2, the geometric tip enhancement  
25 comprising:  
a hydrogen tip termination.
7. The energy conversion device of claim 1, the diamond emitter including a polycrystalline structure with sp<sup>2</sup> bonding.

8. The energy conversion device of claim 1, the diamond emitter including dopants that produce band bending via space charge accumulation.

5 9. The energy conversion device of claim 1, the dopant selected from a dopant group including as nitrogen, phosphorous, and sulfur-hydrogen.

10 10. An electronic cooling device, comprising:  
a cathode comprising at least one emitter structure on a base;  
and  
an anode positioned over and spaced apart from the cathode by a vacuum space,  
a biasing energy supply adapted to bias the cathode to anode  
15 separation, the bias of sufficient potential to cause electron emission from the base electrode through the cathode into the conduction band, then through the vacuum and deposition in the anode;  
the emitter structure including a diamond microtip emitting portion.

20 11. The electronic cooling device of claim 10, the diamond microtip emitting portion including a geometric tip enhancement for enhancing band bending.

12. An electronic cooling device, comprising:  
25 a cathode comprising at least one emitter structure on a base, the emitter structure including a diamond microtip emitter extending upwardly from and formed integral to a diamond substrate having a top surface;

an anode layer spaced apart from the emitter and suspended above the diamond substrate by a first insulating layer extending upwardly from the top surface of the diamond substrate;  
a porous gate positioned above and spaced apart from the diamond  
5 microtip, supported by a second insulating layer extending upwardly from a top surface of the anode layer; and  
a biasing energy supply adapted to bias the anode and the gate separation, the bias of sufficient potential to cause electron emission from the base electrode through the cathode into the conduction band,  
10 then through the vacuum and deposition in the anode.

13. The device of claim 12, the porous gate is constructed in a grid arrangement.

15 14. The device of claim 12, the porous gate is constructed in an annular gate structure adapted to provide appropriate electrical conditions for cathode emission, while also providing a path to the anode.

20 15. The device of claim 12, wherein the bias between the cathode and the anode is maintained at a higher level than that of the bias between the cathode and the gate, but the bias between the cathode and the anode still allows electrons emitted from the cathode to reach the anode.

25

16. A method for energy conversion using a diamond microtip cathode separated from an anode by a vacuum space, the method comprising:

shifting the field emission band with a positive voltage bias on  
30 the anode to narrow the potential barrier width to increase the



probability of quantum tunneling to increase field emission and produce a transfer of thermal energy from the cathode to the anode.

17. The method for energy conversion of claim 16, wherein shifting  
5 the field emission band occurs in the cathode.

18. The method for energy conversion of claim 16, the shifting  
occurring near the base-electrode/cathode interface

10 19. The method for energy conversion of claim 16, wherein shifting  
the field emission band occurs in the vacuum.

20. The method for energy conversion of claim 16, the shifting  
occurring near sp<sup>2</sup>-bonded elements of the polycrystalline structure.

15 21. The method for energy conversion of claim 16, the shifting  
occurring at the cathode/vacuum barrier

22. The method for energy conversion of claim 16, further  
20 comprising:

decreasing the resistance to electron flow between the cathode and anode through the use of a gate electrode designed to extract electrons from the cathode while allowing emitted electrons to bypass the gate.

25

23. An energy conversion structure, comprising:

a biased diamond microtip emitter thermally and electrically connected to a base and spaced from an anode by a vacuum gap, the biased microtip emitter forming curved energy bands adapted to  
30 produce a net energy transfer to an anode.

25.

24. The energy conversion structure of claim 23, the net energy transfer manifest as cooling of the base.

5 25. The energy conversion structure of claim 23, the net energy transfer manifest as power generation with an electrical potential between the anode and the base.

26. A step for improving efficiency for an energy conversion device  
10 using a base electrode and a diamond emitter cathode, the step for improvement comprising:

providing geometric enhancement adapted to increase the local electric field at the interface between the base electrode and the diamond cathode.

15

22. A diamond emitter energy conversion device adapted to provide power to an external circuit, comprising:

a cathode with a microtip structure, the cathode adapted to support a high density of energetic electrons and further adapted to  
20 be electrically connected to the external circuit;

an anode spaced from the cathode and adapted to be electrically connected to the external circuit;

an annular gate electrode adapted to provide a low potential field sufficient for emission of electrons from the cathode tip to the  
25 anode by bypassing the annular gate; and

a biasing energy supply adapted to bias the anode and the gate separation, the bias of sufficient potential to cause electron emission from the base electrode through the cathode into the conduction band, then through the vacuum and deposition in the anode.

30

24. A method for increasing efficiency of energy converters utilizing a thermal differential across a structure including a base connected to a cathode, the cathode separated from an anode by a vacuum space, the cathode including a diamond microtip emitter,  
5 comprising:

enhancing band bending potential of the structure during construction of the cathode and anode structure.

25. The method of claim 24, further comprising:  
10 providing a gate electrodes during construction, the gate electrode adapted to reduce the required voltage for field emission within the structure.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
31 May 2001 (31.05.2001)

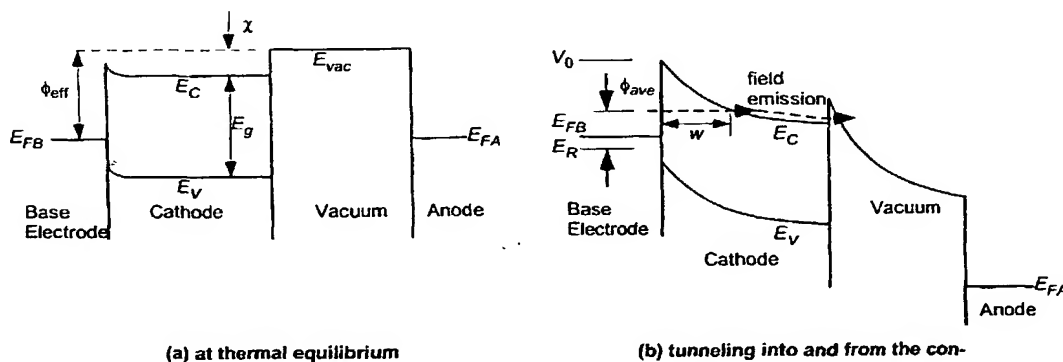
PCT

(10) International Publication Number  
**WO 01/39235 A2**

- (51) International Patent Classification<sup>7</sup>: **H01J** Nashville, TN 37215 (US). **DAVIDSON, Jimmy, Lee** [US/US]; 219 River Oaks Road, Brentwood, TN 37027 (US). **KANG, Weng, Poo** [MY/US]; 1222 Spring Creek Drive, Nashville, TN 37209 (US).
- (21) International Application Number: **PCT/US00/40921**
- (22) International Filing Date:  
18 September 2000 (18.09.2000) (74) Agent: **SHOUSE, Emily, A.**; Wadley & Patterson, Suite 2020, 414 Union Street, Nations Bank Plaza, Nashville, TN 37219 (US).
- (25) Filing Language: English
- (26) Publication Language: English (81) Designated States (*national*): CN, JP, US.
- (30) Priority Data:  
60/154,500 17 September 1999 (17.09.1999) US (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
- (71) Applicant (*for all designated States except US*): **VAN-  
DERBILT UNIVERSITY** [US/US]; Office of Technology  
Transfer, 405 Kirkland Hall, Nashville, TN 37240 (US).
- Published:  
— Without international search report and to be republished  
upon receipt of that report.
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **FISHER, Timothy,  
S.** [US/US]; 2508 Essex Place, Nashville, TN 37212 (US).  
**STRAUSS, Alvin, M.** [US/US]; 2302 Valley Brook Road,

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

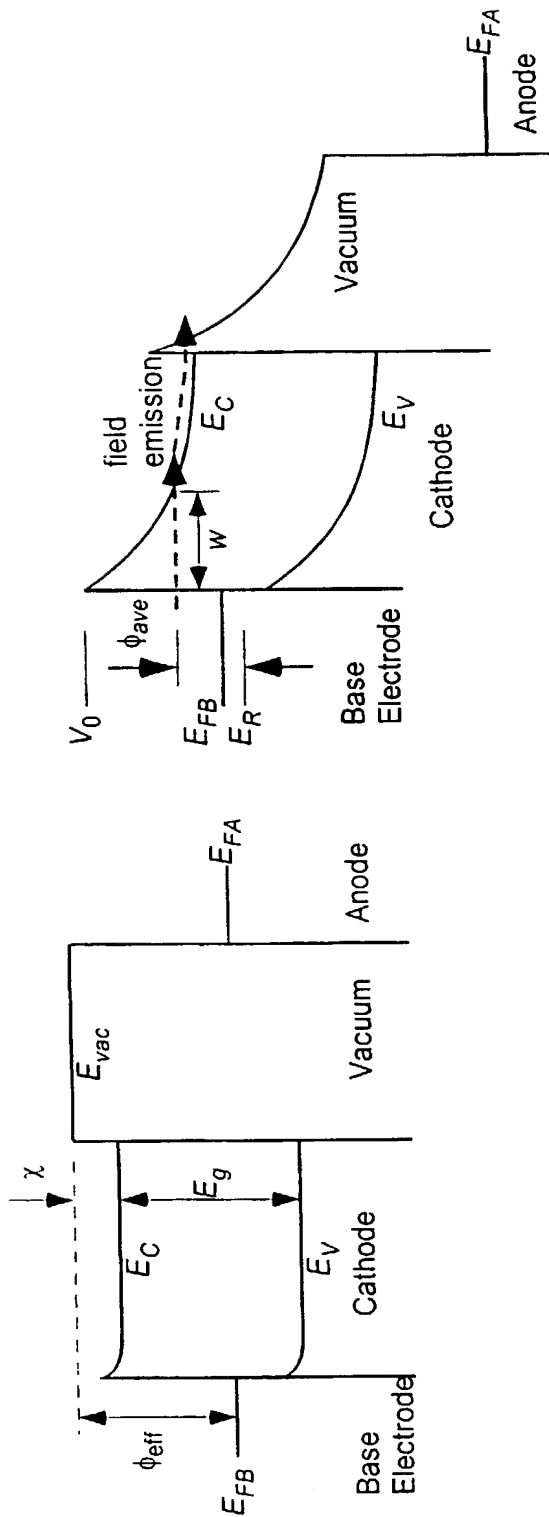
(54) Title: THERMODYNAMIC ENERGY CONVERSION DEVICES AND METHODS USING A DIAMOND-BASED ELECTRON EMITTER



Band diagrams for field emission from diamond cathodes. (a) Unbiased state. (b) Under bias with tunneling into and from diamond's conduction band.

(57) Abstract: An energy conversion device adapted to enhance field emission including a diamond emitter adapted to utilize band bending to emit a high-energy distribution of electrons to produce an energy conversion effect. The invention teaches the use of band bending to enable or enhance energy conversion. Three different band bending methods are described. The first involves the use of geometric tip enhancement. The second involves the inclusion of graphite-like (sp<sup>2</sup>-bonded) molecular structures within the polycrystalline film. These two features produce band bending via small geometric features, such as tips and filaments, as governed by electrostatic theory. The third involves the incorporation of p- and n-type dopants that produce band bending via space charge accumulation.

WO 01/39235 A2



(a) at thermal equilibrium

(b) tunneling into and from the conduction band under bias

Figure 1. Band diagrams for field emission from diamond cathodes. (a) Unbiased state. (b) Under bias with tunneling into and from diamond's conduction band.

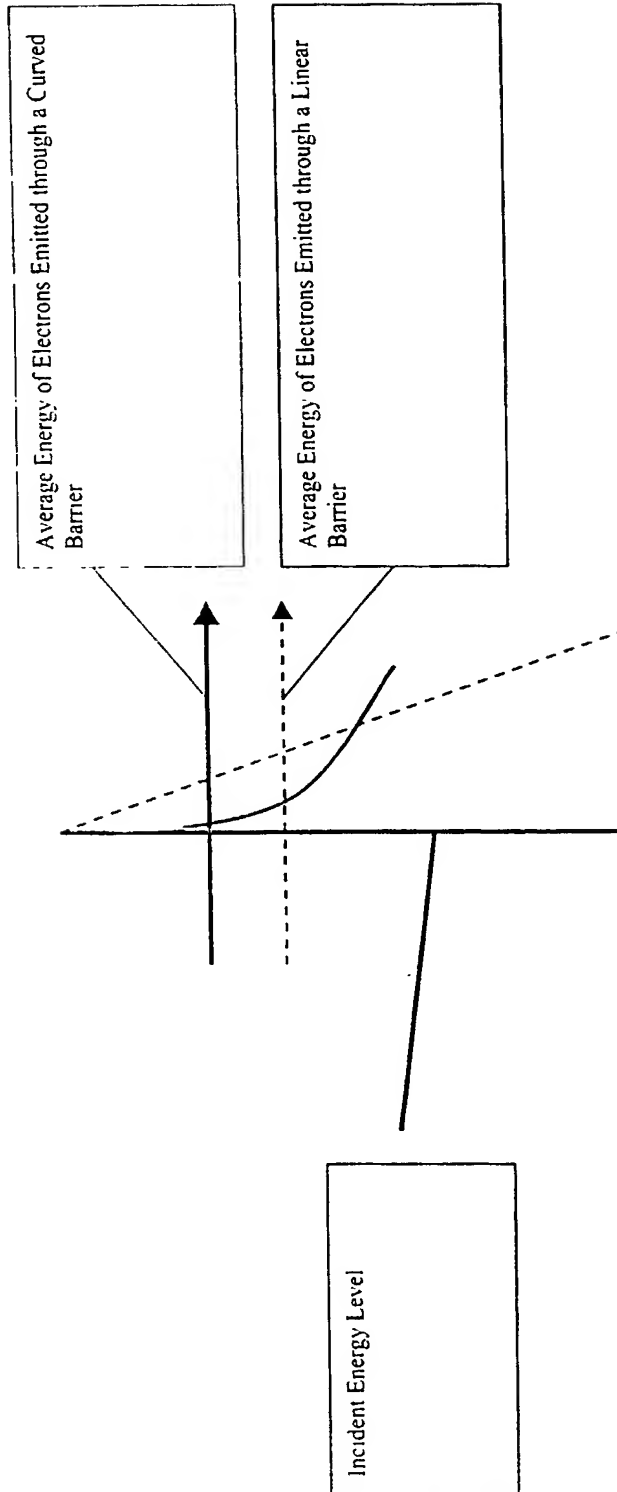


Figure 2. Average electron energies for field emission with and without band bending

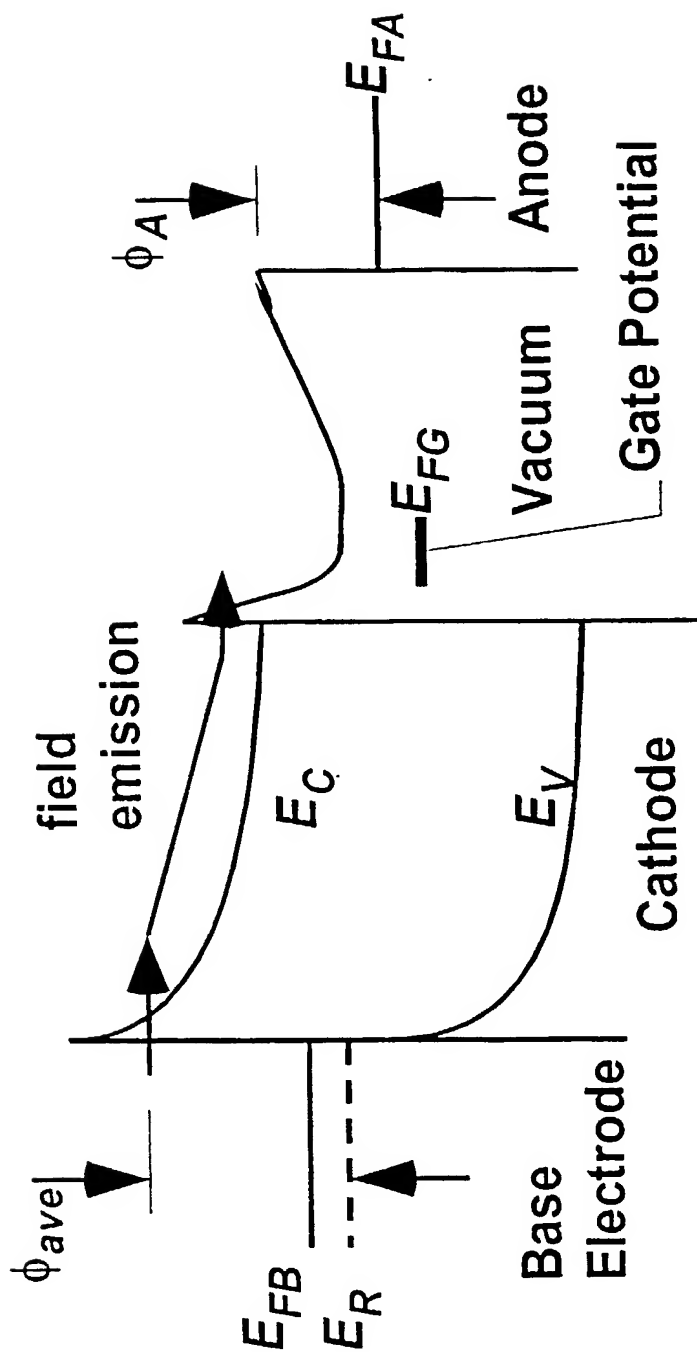


Figure 3. Refrigeration enhancement using a gate electrode. (a) Band diagram for field emission from a gated diamond cathode in the biased state.

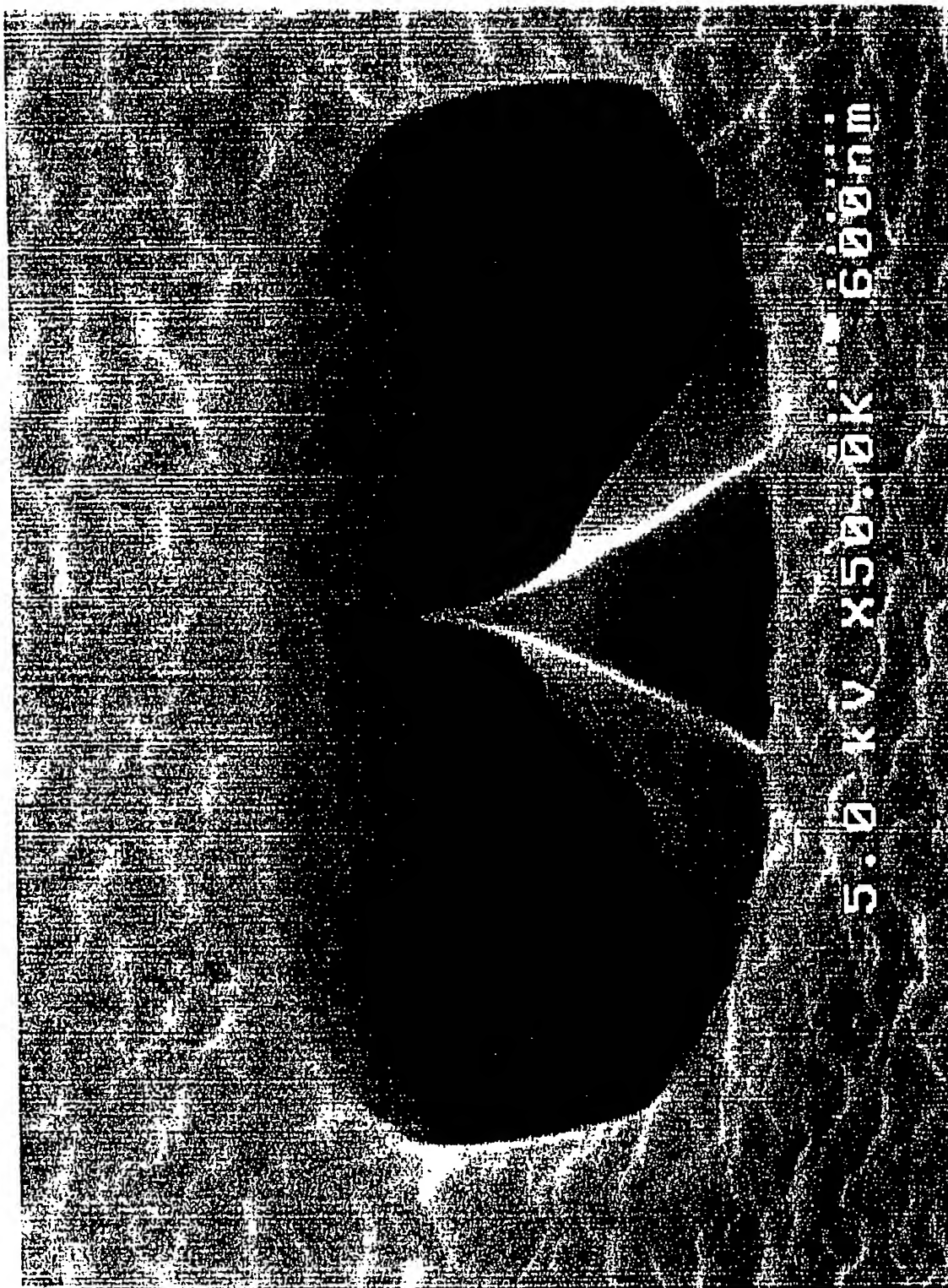


Figure 4. Annular gate structure surrounding a diamond-tip emitter cathode.



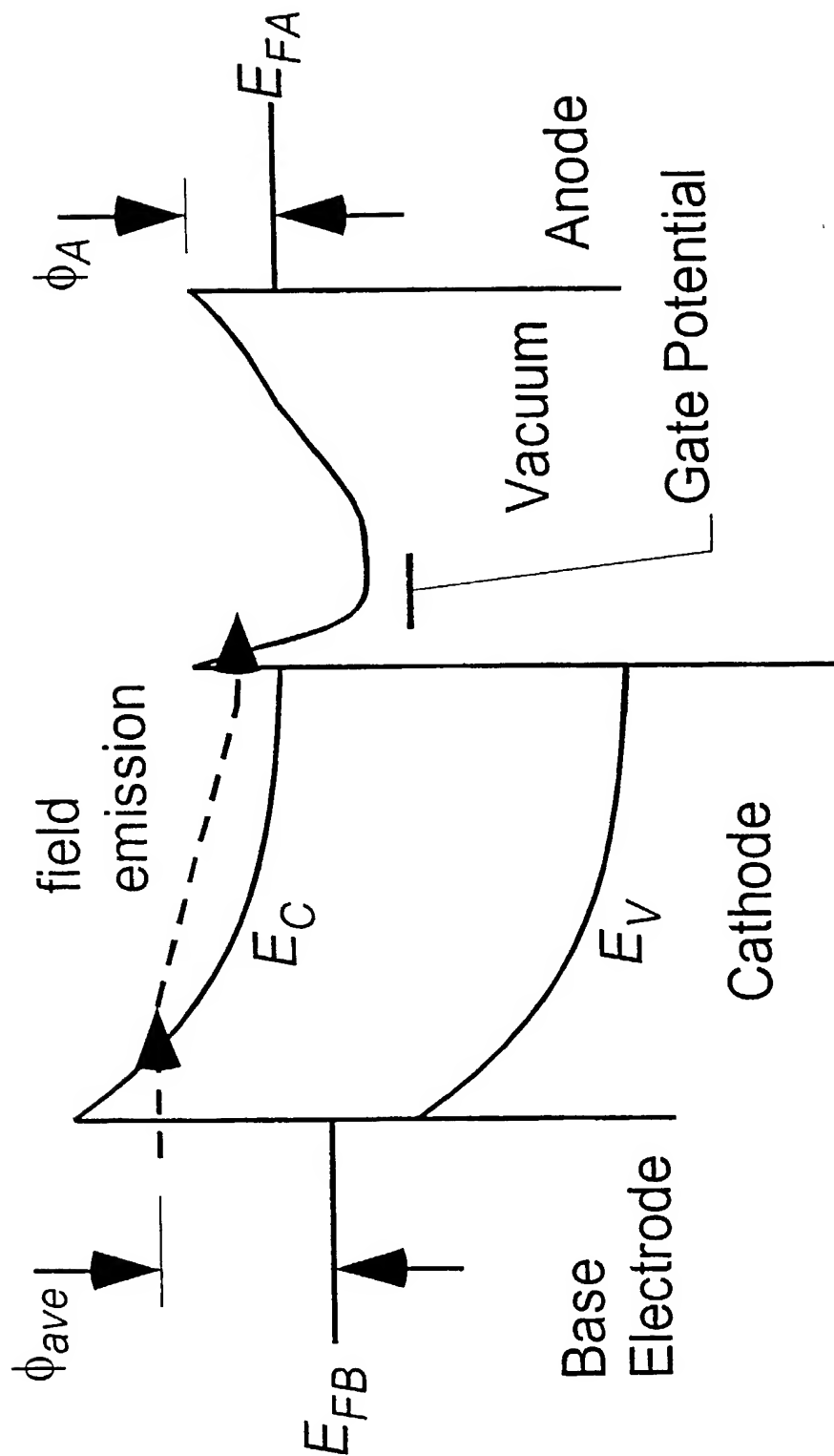


Figure 5. Band diagram for a gated power generation device.

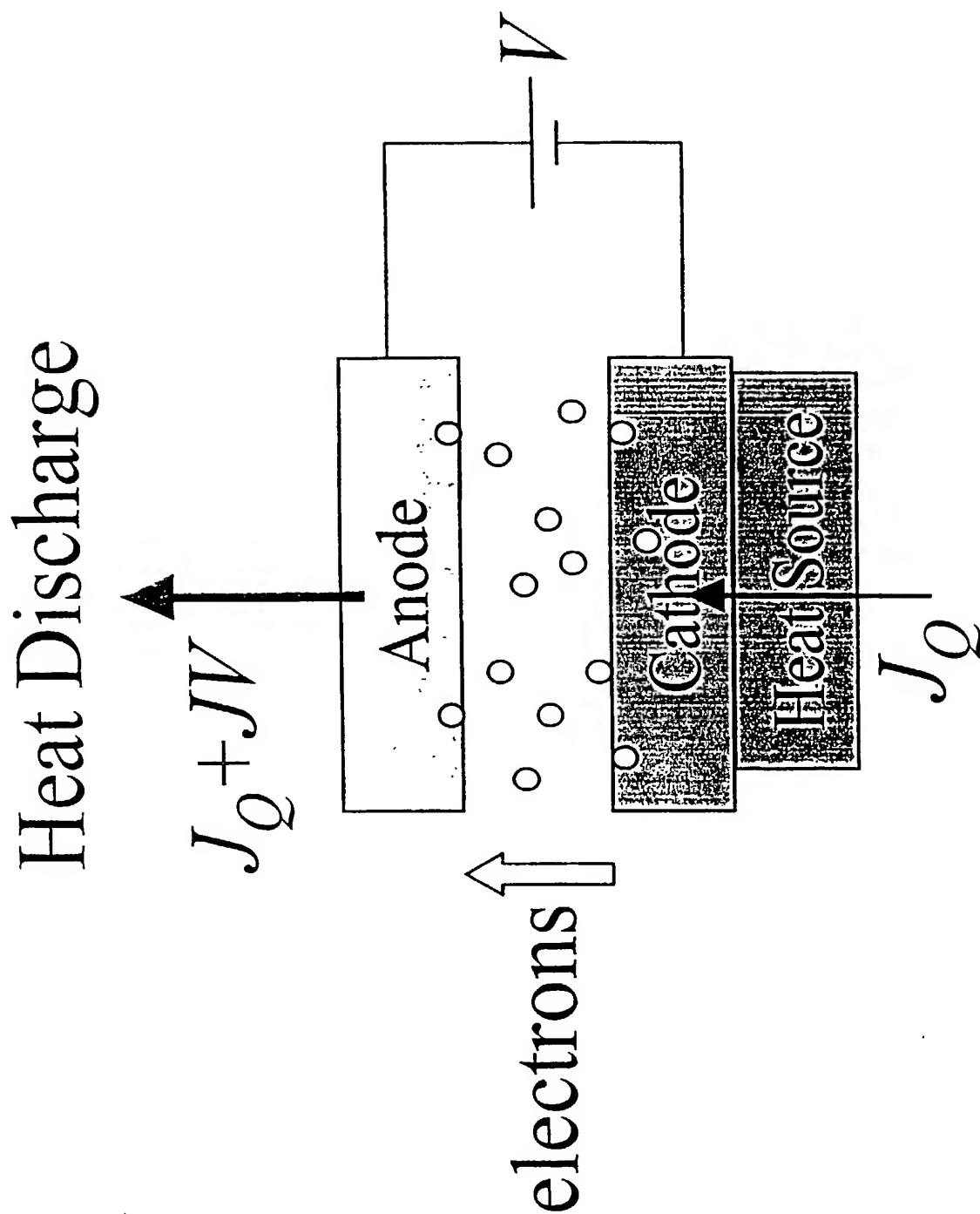


Figure 6. Schematic of a direct refrigeration device.

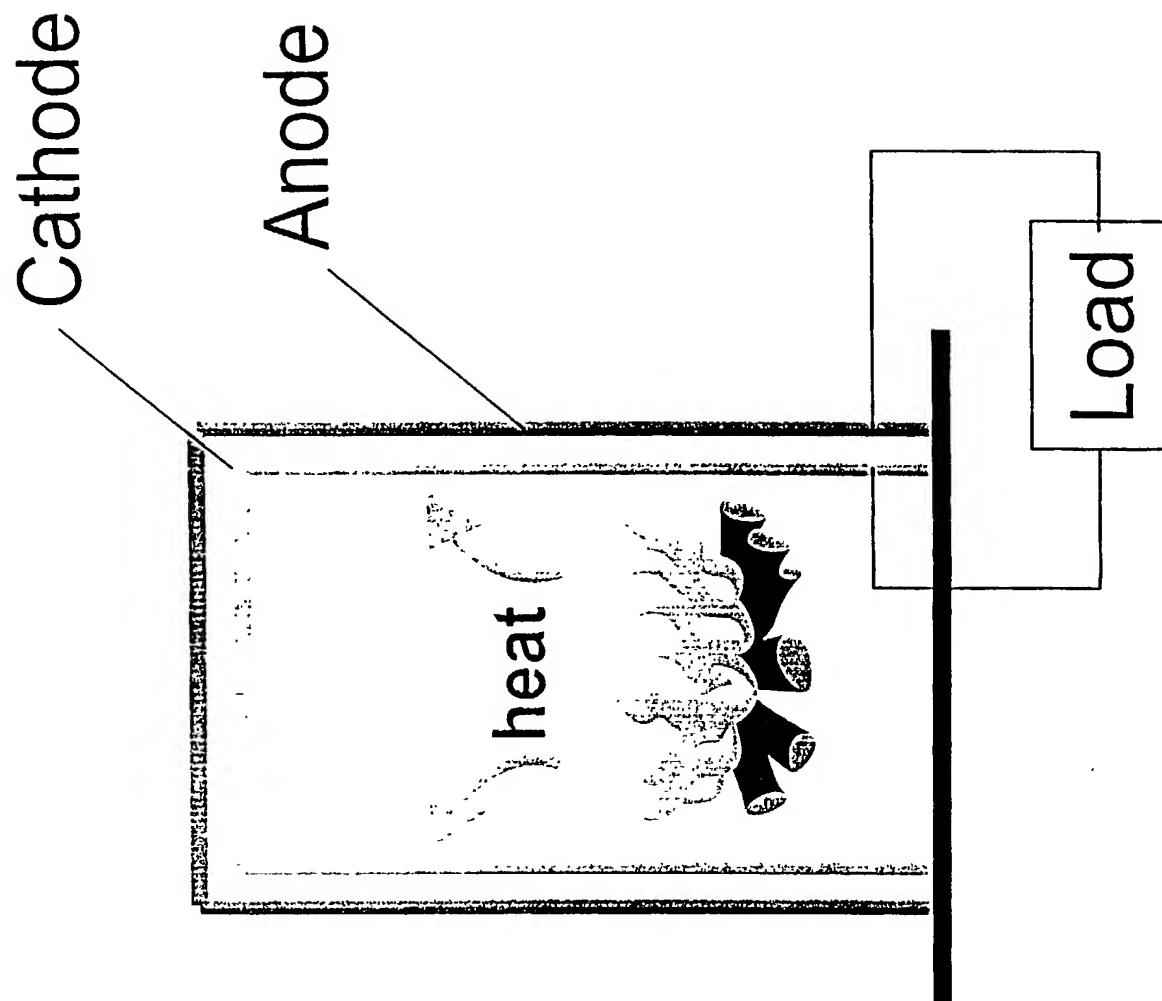


Figure 8. Schematic of a direct power generation device.

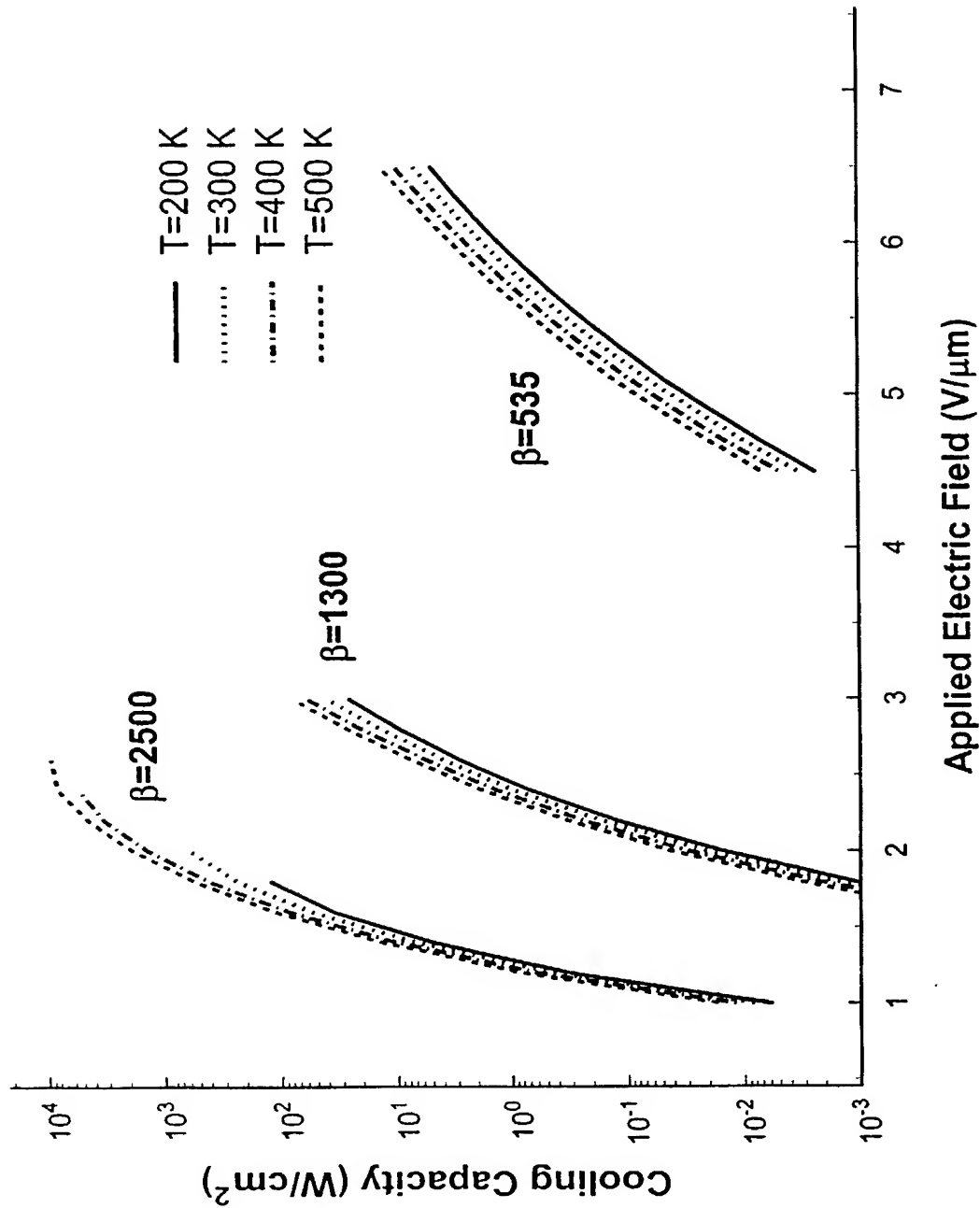


Figure 7. Predicted cooling capacity as a function of applied electric field, field enhancement factor  $\beta$ , and temperature.

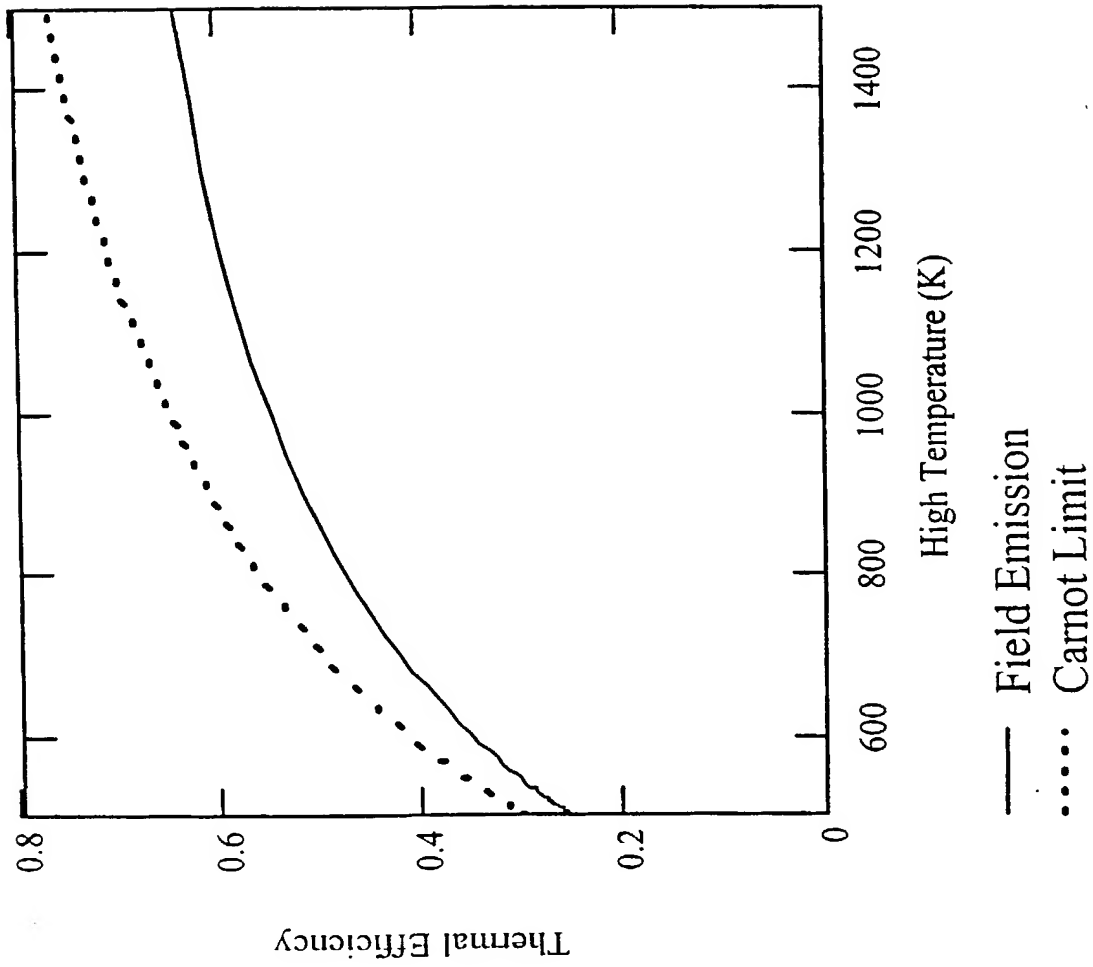


Figure 9. Predicted thermal efficiency of standalone power generation by field emission as a function of hot-side temperature.

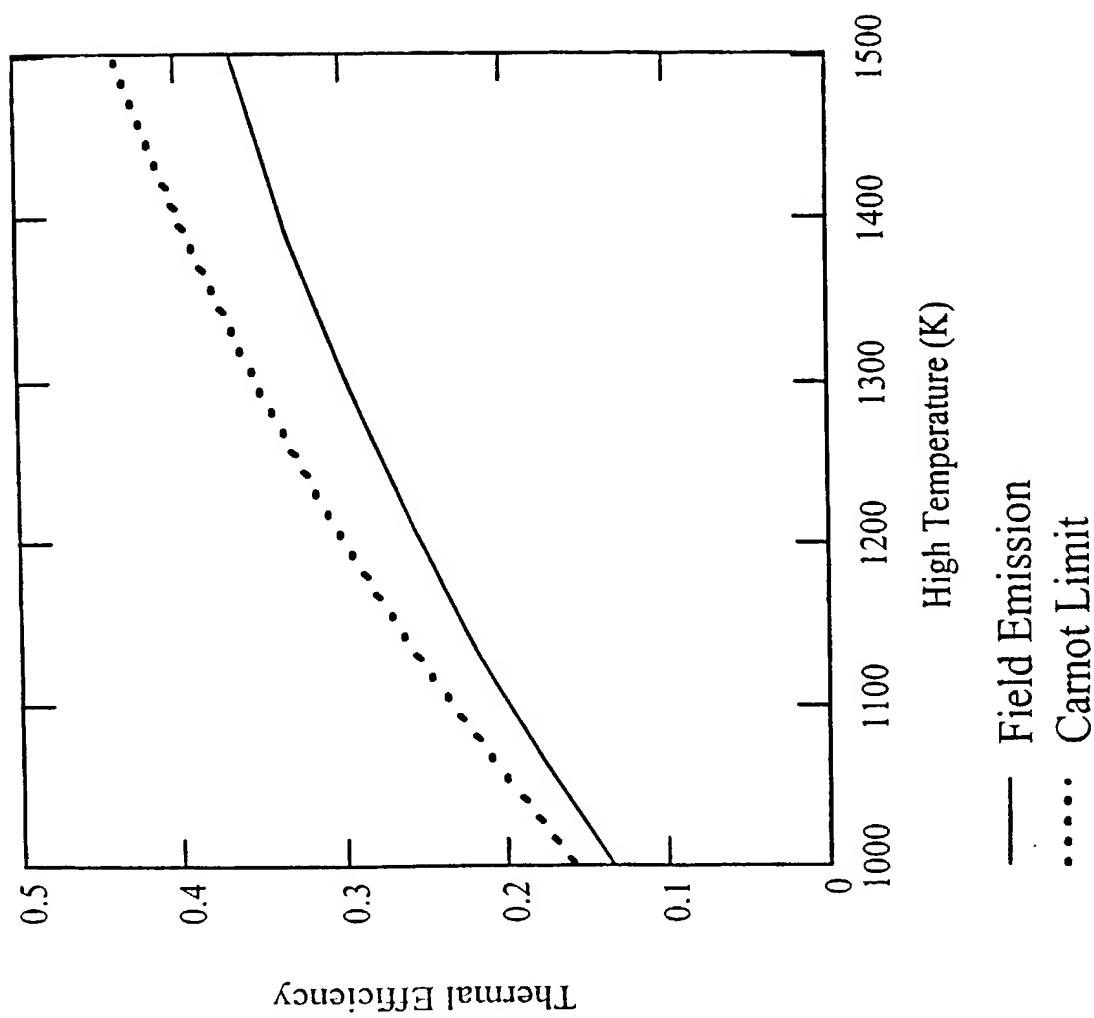


Figure 10. Predicted thermal efficiency of topping cycle power generation by field emission as a function of hot-side temperature.

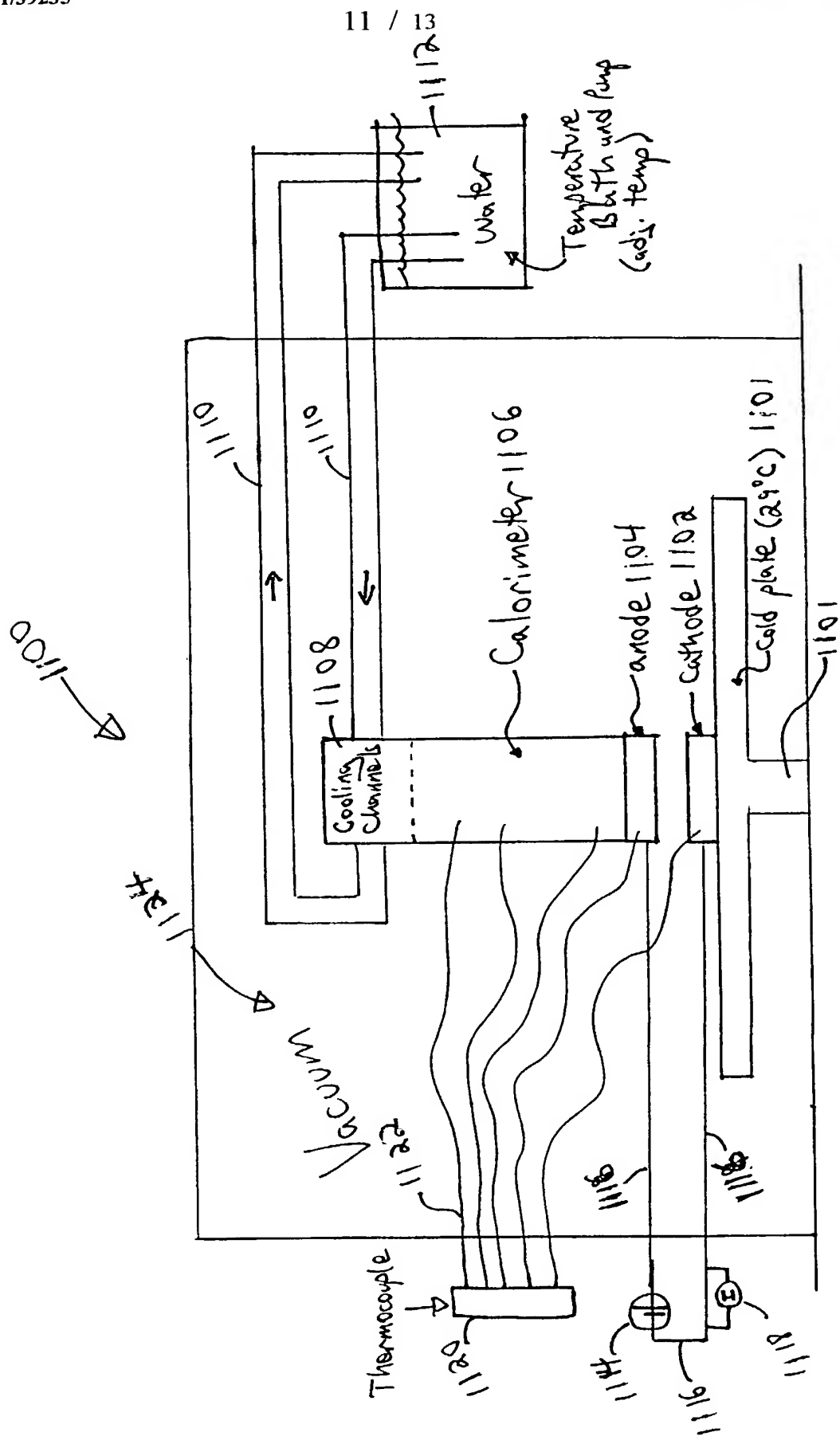


Fig. 11

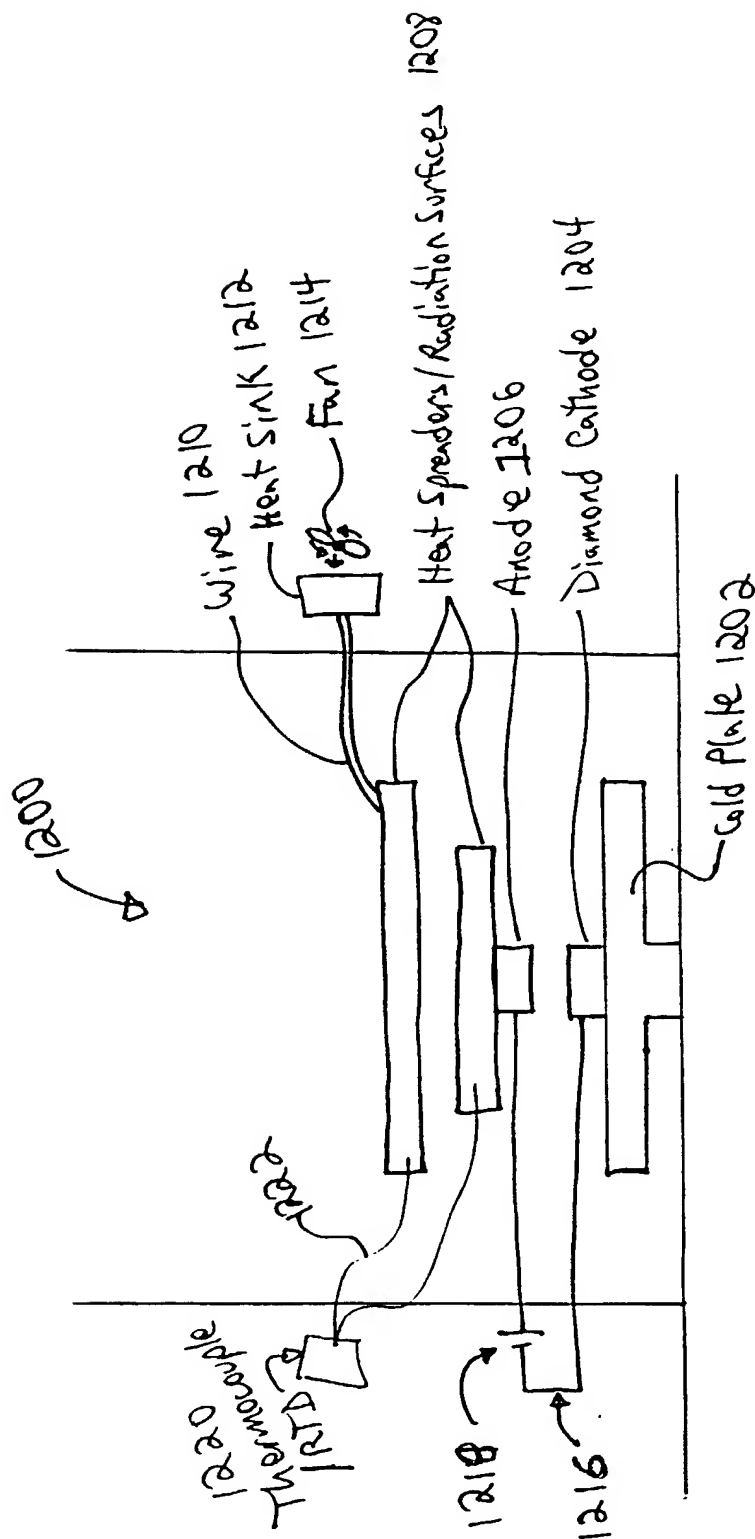


Figure 12



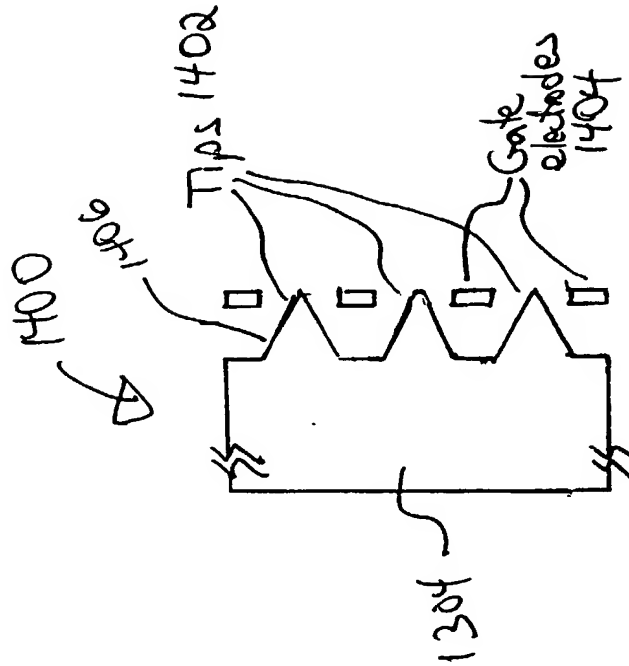


Figure 14

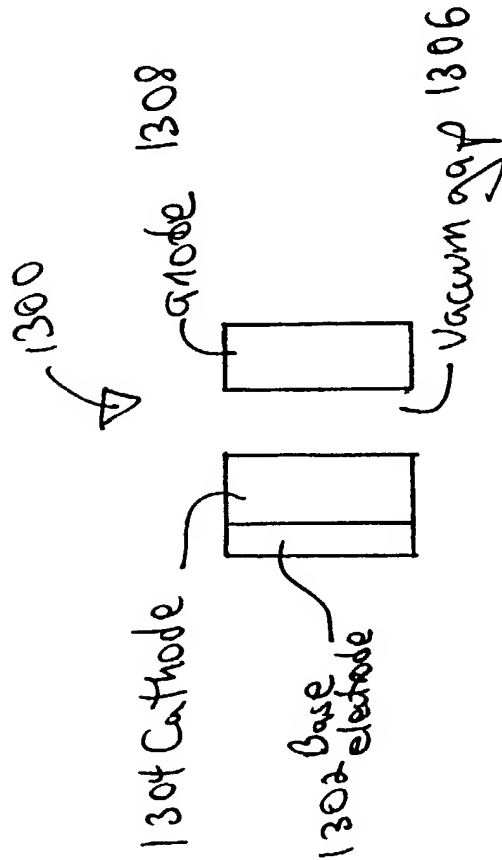


Figure 13

## **DECLARATION AND POWER OF ATTORNEY**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled "Thermodynamic Energy Conversion Devices And Methods Using A Diamond-Based Electron Emitter" the specification of which was filed on 18 September 2000 as PCT International Application Number PCT/US00/40921.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. §1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the nation or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate

having a filing date before that of the application on which priority is claimed:

Prior Foreign Appln. No.	Country	Foreign Filing Date	Priority Not Claimed
PCT/US00/40921		09/18/2000	<input type="checkbox"/>

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I hereby appoint the following attorneys and agents to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

Mark J. Patterson (Reg. No. 30,412)  
 I. C. Waddey, Jr. (Reg. No. 25,180)  
 Edward D. Lanquist, Jr. (Reg. No. 33,729)  
 Lucian Wayne Beavers (Reg. No. 28,183)  
 Emily A. Shouse (Reg. No. 44,336)  
 David B. Pieper (Reg. No. 42,998)  
 Richard S. Myers, Jr. (Reg. No. 42,022)  
 Larry W. Brantley (Reg. No. 46,052)  
 Guy W. Hensley (Reg. No. 41,831)  
 Douglas W. Schelling (Reg. No. 48,335)

Customer No. 23456

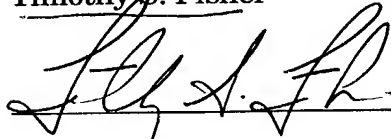
Please direct all correspondence to **Emily A. Shouse** at the address and telephone number below.

Emily A. Shouse  
Wadley & Patterson  
414 Union Street, Suite 2020  
Bank of America Plaza  
Nashville, TN 37219  
(615) 242-2400

Full name of joint Inventor:

1-00  
Timothy S. Fisher

Inventor's signature:



Date:

4/15/02

Residence:

2508 Essex Place <sup>TN</sup>  
Nashville, Tennessee 37212

Citizenship:

U.S.

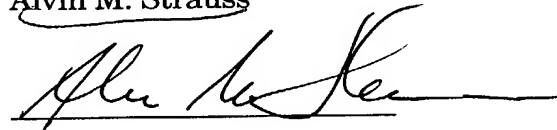
Post Office Address:

2508 Essex Place  
Nashville, Tennessee 37212

Full name of joint Inventor:

2-00  
Alvin M. Strauss

Inventor's signature:



Date:

4/15/02

Residence:

2302 Valley Brook Road <sup>TN</sup>  
Nashville, Tennessee 37215

Citizenship:

U.S.

Post Office Address:

2302 Valley Brook Road  
Nashville, Tennessee 37215

3-00

Full name of joint Inventor:

Jimmy Lee Davidson

Inventor's signature:

Jimmy Lee Davidson

Date:

4-15-02

Residence:

219 River Oaks Road <sup>TN</sup>  
Brentwood, Tennessee 37027

Citizenship:

U.S.

Post Office Address:

219 River Oaks Road  
Brentwood, Tennessee 37027

4-00

Full name of joint Inventor:

Weng Poo Kang

Inventor's signature:

Weng Poo Kang

Date:

4-15-02

Residence:

~~1222 Spring Creek Drive~~ <sup>TN</sup> 108 Trace Park Ct. E  
~~Nashville, Tennessee 37209~~ Nashville, TN 37221

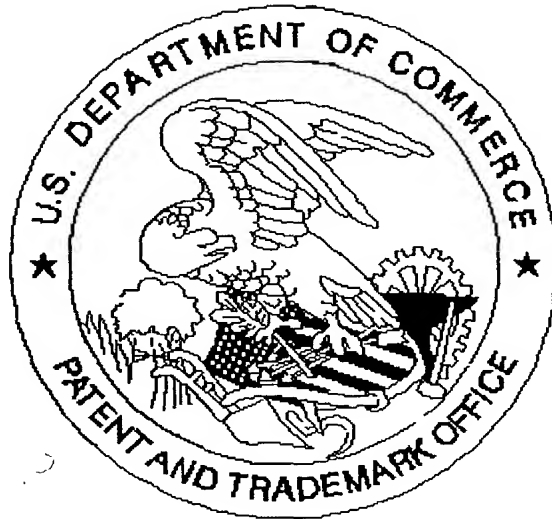
Citizenship:

~~MY~~ U.S.

Post Office Address:

~~1222 Spring Creek Drive~~ 108 Trace Park Ct. E  
~~Nashville, Tennessee 37209~~ Nashville, TN 37221

United States Patent & Trademark Office  
Office of Initial Patent Examination -- Scanning Division



Application deficiencies found during scanning:

☐ Page(s) \_\_\_\_\_ of \_\_\_\_\_ were not present  
for scanning. (Document title)

☐ Page(s) \_\_\_\_\_ of \_\_\_\_\_ were not present  
for scanning. (Document title)

☒ Scanned copy is best available. *Some drawings are dark.*